

POLYNUCLEAR AROMATIC HYDROCARBONS
IN URBAN ATMOSPHERES IN ONTARIO

Air Quality Laboratory
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December 1971

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ONTARIO MINISTRY OF THE ENVIRONMENT
LABORATORY SERVICES BRANCH

POLYNUCLEAR AROMATIC HYDROCARBONS
IN URBAN ATMOSPHERES IN ONTARIO

Part 1: Interim Report

by E.G. Adamek, Ph.D.

Toronto, December 30, 1971

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The aim of this report is to cover the progress made during the first year of work on this project, to indicate the direction taken in pursuit of the objectives of this project, the analytical methods adopted and developed, and the results for the first 5-month period of a one-year survey of this type of air-pollutants in urban areas in Ontario. This annual report supplements the three quarterly progress reports issued earlier this year (1) but also includes portions of these which are essential for a comprehensive summary of the progress made on the above project. Work done during this period outside the scope of this project, or which was considered to be of little importance for its objectives, is not included in this report.

Objectives of Work:

In line with the general aim of developing feasible analytical methods for the routine determination of carcinogenic air pollutants, and of monitoring these pollutants on Hi-Vol filters, the following tentative objectives had been proposed for the approximate period of two years:

- a) To explore and establish methods for the reliable, fast and economical determination of polynuclear aromatic hydrocarbons on Hi-Vol Filters. Particular attention to be directed toward the determination of those air-pollutants which appear most prevalent and representative of this group, and which are most potent as carcinogens.
- b) To initiate development of these methods for use on a routine basis for analyzing larger numbers of samples, such as needed for analytical surveys.
- c) To initiate and carry out a programme for studying the occurrence and distribution of these compounds in the air of major industrial and population centres in Ontario.

Progress toward Objectives:

1) Abstract

During the approximately one-year period, work had been concentrated on the following short-term objectives:

- a) A study was made on the extraction of organic material from Hi-Vol filters by determining the suitability of a number of organic solvents as extractants; also, the usefulness of ultrasonic techniques for extraction, as compared with the Soxhlet extraction, was investigated.
- b) A study was made on the chromatographic separation of benzo(a)pyrene and benzo(k)fluoranthene from the extract of Hi-Vol filters. An efficient and fast method was adapted for separating on a routine basis both of these compounds from the remainder of other organic material in the filter extract. This separation technique requires the subsequent application of an approximation method developed by Monkman for estimating the concentrations of these compounds by spectrophotofluorometry. In addition, we are working on a tentative method by which these compounds can be separated from each other, which permits their direct determination, independently from each other, for the first time.

- c) A spectrophotofluorometric method was successfully adopted for the estimation of benzo(a)pyrene and benzo(k)fluoranthene in mixtures as contained in the fractions from the liquid-phase chromatographic separation. The time-consuming and rather complex calculations involved were computerized for greater speed and efficiency; this proved to be important for handling the large number of data produced for developing the analytical methods and carrying out the subsequent survey on Hi-Vol filters.
- d) A programme for studying the occurrence and distribution of polynuclear hydrocarbons in urban air in Ontario was initiated and eight cities were selected for monitoring benzo(a)pyrene and benzo(k)fluoranthene over the period of one year. Accordingly, analyses for these two compounds are now well under way and the results for the first 5-month period, commencing with the month of July 1971, are presented here together with some preliminary comments on these data. Upon completion of this programme, a more comprehensive report will be prepared, which will include a discussion of the data in the light of topographical and meteorological influences.

2) Introduction:

The cancer-producing property of soot was known in England already at the end of the last century by the experience of the "chimney sweeps". It took until 1933, after benzo(a)pyrene had been isolated from soot and its structure elucidated that the carcinogenicity of this compound was first demonstrated on experimental animals (2).

Benzo(a)pyrene (BaP) turned out to be the most powerful carcinogenic known (3)(4) and is generally formed in combustion processes of carbonaceous material. In subsequent years, the particulate matter in urban air has been found to contain BaP and other polynuclear hydrocarbons, some of which showed also carcinogenicity to both laboratory animals and man (5)(6). Over the last two decades, the number of studies on the nature and quantitative occurrence of these compounds in the air of mainly North-American and European cities has steadily increased.

In these studies a considerable number of analytical methods has been used, ranging from gas-chromatographic and u.v.-visible absorptionmetric to fluorometric and mass-spectrographic methods. However, because of a variety of short-comings,

none of these methods has yet been accepted by the American Society for Testing and Materials (ASTM) as a permanent "Standard Method".

Gas-chromatographic methods suffered invariably under suspicion of thermal degradation of the high-boiling polynuclear hydrocarbons at the high column temperatures required(7).

Absorptiometric methods have widely been used and the 399-402-405 nm absorption has been preferred for the determination of BaP (8). However, serious disadvantages have critically limited the usefulness of these methods: Apart from only a weak response at the above wavelength (9), the absorption of BaP was found to be subject to interference by benzo(k)fluoranthene (10) which by having the same chromatographic retention time, was recently shown to accompany BaP almost invariably as an air-pollutant (11). This finding has cast doubt upon the validity of earlier results from analyses of BaP on Hi-Vol filters.

More recently, much painstaking and time-consuming efforts have been made to develop methods by which separation of the

polycyclic hydrocarbons could be accomplished (12)(13) in order to avoid such interferences. By rather complex chromatographic procedures, involving column and two-dimensional thin-layer chromatography, sufficient fractionation of the Hi-Vol filter extracts was achieved to permit a more accurate absorptiometric analysis of some of the components separated. In the absence of better methods, one absorptiometric method had been temporarily included as a "Tentative Standard ASTM - Method" (14) for the interim period ending November 1971. Unfortunately, all the methods developed proved to be very tedious, impracticable and particularly unsuitable for the purpose of monitoring these pollutants in air: A single BaP-determination carried out by an experienced worker requires reportedly as much as 2 days (12) (14). In addition, owing to the inherently low sensitivity of absorptiometry compared to fluorometry, large sample sizes of about 10 Hi-Vol filters are required per analysis, which renders this method virtually useless for large scale surveys. The requirement of expensive spectrograde solvents in amounts of several liters per analysis is also a great disadvantage, especially since they are unlikely to be recoverable for repeated use. Finally, a study on the

comparison of analytical methods for trace analysis of polycyclic hydrocarbons (15) concludes with the recommendation to abandon the absorptiometric methods entirely in favour of the more promising and more sensitive fluorometric methods. Nevertheless, the absorptiometric technique did provide in 1961 the first data for the occurrence of BaP and some other hydrocarbons in urban air in Ontario (16). These data are still significant since they permit a comparison of the areas involved even if the absolute values of the data obtained seem now somewhat in question.

Since the last few years, fluorometric techniques for determining polynuclear aromatic hydrocarbon have been subject to intensive study, whereby the overwhelming advantages of these techniques over the absorptiometric approach became more and more evident. The sensitivity of fluorometric methods is about 300 - 3000 times higher, and consequently much smaller sample sizes (of only small fractions of a Hi-Vol filter) are required. Fluorescence, in general, is also a more specific property of matter than absorption since it is exhibited by only relatively few groups of compounds, including the polynuclear aromatic

compounds. Thus, in principal, fluorometric methods may require less scrupulous and less elaborate separation techniques, which can result in considerable time and labour savings. A method was also developed which combines both the absorptiometric and the fluorometric techniques for the determination of a number of polynuclear hydrocarbons (17); although apparently more accurate, this method still involves the necessity for cumbersome and elaborate chromatographic separation.

A break-through was finally achieved when Monkman and co-workers succeeded in the much more rapid separation of BaP and BaF from all other components in the filter extracts by simple column chromatography (11). Followed by fluorometric analysis of the chromatographic fractions obtained, thereby utilizing two different excitation wave-lengths, the estimation of these two compounds became possible with reasonably close approximation.

The use of mass-spectrometry which, of course, still requires a preceding chromatographic separation process, is presently investigated by various research groups. Although some preliminary results may look reasonably promising, the cost of about \$50,000 for the mass-spectrograph plus space and

labour requirements, put this technique, at least presently, beyond the means of this laboratory.

In conclusion of the above and in line with the objectives of the present work, we therefore decided to use the fluorometric technique for the determination of polynuclear aromatic hydrocarbons in Hi-Vol filters. Nevertheless, the problem of the complexity of separating even a relatively limited number of these compounds from each other to enable their fluorometric determination, still seemed to lead to prohibitive time, labour and equipment requirements. According to our extensive literature study, only the technique developed by Monkman and co-workers (11) for the more rapid estimation of BaP and BkF seemed to offer the potential for a sufficiently economical method which would enable us to monitor these pollutants on a routine basis.

However, it was mainly for fundamental considerations that we felt that for the present work the primary effort should be directed toward establishing a reliable, fast and economical method for the determination of benzo(a)pyrene. The reasons for selecting this compound from all other polycyclic hydrocarbon air pollutants have been established by previous investigators (18), which can be summarized as follows:

- a) Benzo(a)pyrene has proved to be the most potent carcinogen of those known to date. The presence of this compound as a pollutant in air is widespread and its origin has been traced to a great many sources which include; Incineration, burning and combustion processes of carbonaceous material; industrial emissions, such as from the chemical industry, certain manufacturing industries, and coal-, petroleum- and natural gas-fired power plants; automotive, jet engine and other engine exhausts; personal activities, such as barbecuing, burning of human refuse and foliage, cigarette smoking, etc.
- b) BaP has frequently been used as an "index" of carcinogenic potential for comparison with other members of the polynuclear hydrocarbon group.
- c) It could serve as a semiquantitative index of the presence in air of other polynuclear hydrocarbons, some of which are also known to be carcinogenic.

In view of these considerations, any major attempts to include other polynuclear hydrocarbons in our analytical methods development programme should be of secondary priority to the quantitative determination and survey of BaP on Hi-Vol filters. An exception was made in our methods development programme by including benzo(k)fluoranthene for which carcinogenic properties have not been established.

Recent studies by Monkman (11) have shown that this compound was present wherever BaP was formed. Since separation of these two compounds could not be achieved without very elaborate and time-consuming procedures, the estimation of both of these compounds became desirable in order to avoid erroneously high values for BaP. Of course, with BkF being a representative member of the polynuclear hydrocarbon group, its analysis could also provide further insights into the occurrence of this important group of air pollutants in general.

3) Extraction of Hi-Vol Filters

a) Solubilities of Polycyclic Aromatic Hydrocarbons

A study was made to investigate the efficiency of various organic solvents for the extraction of the organic compounds from Hi-Vol Filters and, in particular, for the extraction of the polynuclear hydrocarbon compounds.

The solubilities of a number of these compounds were determined by mixing 2 - 5 mg. quantities with gradually increasing amounts of the solvent to be investigated until complete solution was accomplished; the solubilities of a number of these hydrocarbon compounds in various solvents at room temperature are shown in Table I.

TABLE I
Solubilities of Polycyclic Hydrocarbons in Organic Solvents

Solvent	Anthracene (3-ring)	Chrysene (4-ring)	Pyrene (4-ring)	Benzo(a)pyrene (5-ring)	Fluoranthene (5-ring)
	%	%	%	%	%
Benzene	1.31	0.62	10.7	5.5	28.6
Toluene	0.83	n.d.	12.1	n.d.	23.8
Dioxane	0.53	0.54	15.1	9.1	37.1
Cyclohexane	0.14	0.025	1.5	0.14	3.5
n-Hexane	0.12	n.d.	1.1	n.d.	2.1
n-Pentane	0.11	0.018	0.8	0.031	1.3
Iso-Propanol	0.06	n.d.	0.5	n.d.	1.3

From the results in Table I it is evident that a wide range of solubilities exist for the various polynuclear hydrocarbons in the same solvent. However, it is not possible to deduce a direct relationship between solubility and number of aromatic rings in the molecule, althouth the larger molecules are generally more soluble. By comparing the solubilities of the same polycyclic hydrocarbon compound in different organic solvents, a similar wide range of solubilities is noticeable.

Although these solubilities are, generally, large enough to ensure that the total of the polynuclear hydrocarbons on Hi-Vol filters would be extracted by the cyclic or aromatic solvents, the solubilities in aliphatic solvents, such as n-pentane and n-hexane, could become critically small for achieving quantitative extractions. Thus, acceptable solvents for the extraction of Hi-Vol filters would include: benzene, toluene, cyclohexane and dioxane.

b) The Effect of Solvents on Fluorescence

While studying the absorption characteristics of various polynuclear aromatic hydrocarbons, we observed that the intensities seemed to be unaffected by the type of solvent used (1). By contrast, an investigation of the excitation and emission spectra of these compounds showed that the intensity of the fluorescence varied significantly with the nature of the solvent.

The change in emission intensity of BaP at 410 nm was established over the concentration range of 0.01 to 1.0 ppm for several organic solvents. The results shown in Figure 1 indicate that the intensity of BaP was 2 - 7 times stronger by using aromatic or other cyclic solvents than when aliphatic solvents were used. Thus, considerable advantage could be derived in fluorometric analysis by selecting a solvent which enhances the instrument response and thereby increases the sensitivity of the analytical method. Such solvents include cyclohexane, benzene, toluene and dioxane, which also have shown high dissolving power for polynuclear hydrocarbons.

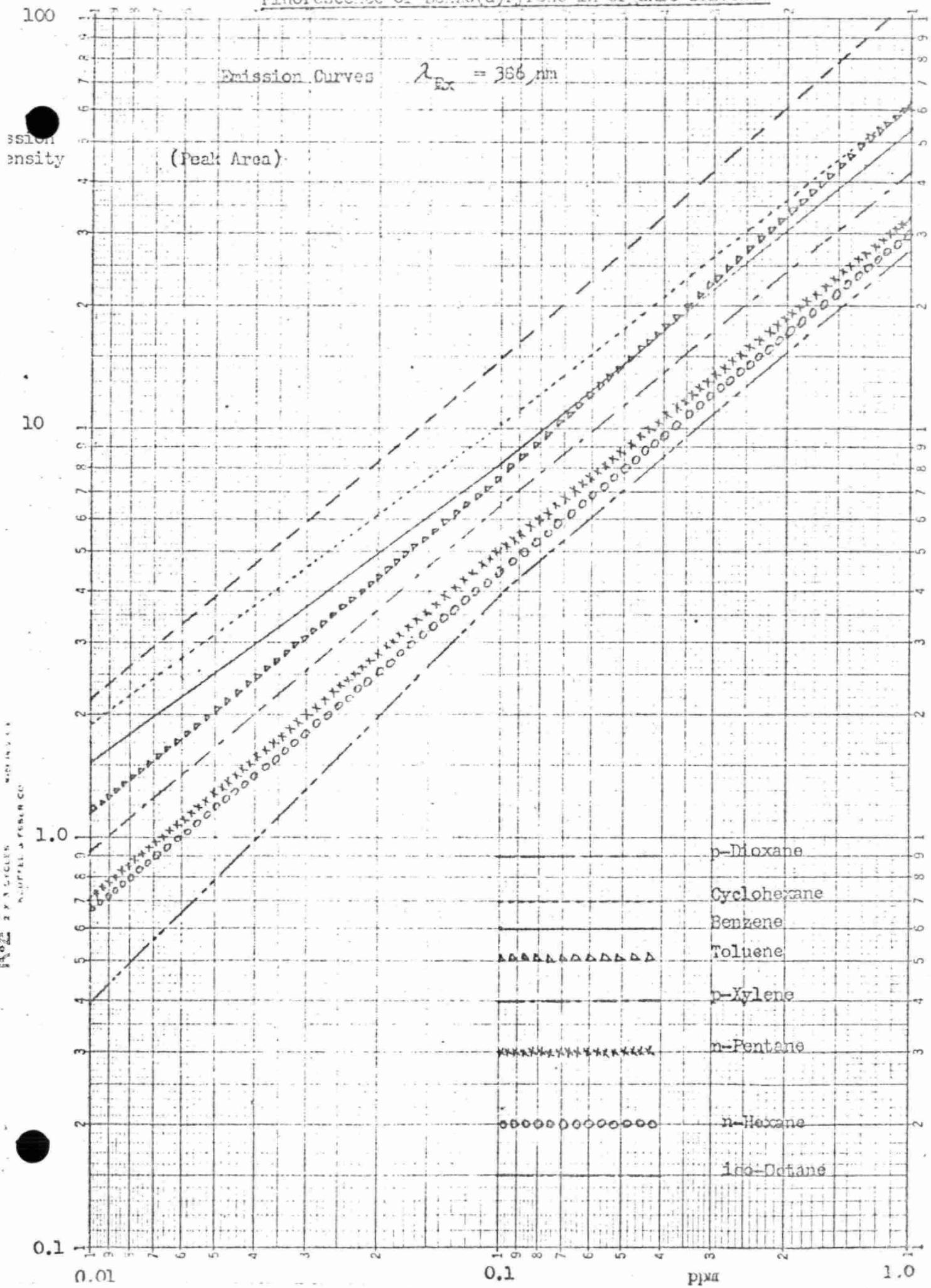
c) Soxhlet Extractions of Hi-Vol Filters

After having established the solubilities of some polynuclear hydrocarbon compounds in a variety of organic solvents and then the effect of these solvents on the fluorescence of such compounds, we began to investigate the efficiency of these solvents for actual Hi-Vol filter extractions.

i) Total "Organics":

Soxhlet extractions with six different solvents were made using a composite of Hi-Vol filters originating from Malton, Station #4, as shown in Table 2. After extraction at rapid

Figure I
Fluorescence of Benzo(a)Pyrone in Organic Solvents



reflux for periods of 12 hours, aliquote portions of the extracts were used for establishing the weight of extracted material after evaporation of the solvent.

TABLE 2
Composite Hi-Vol Filter, Malton Station #4

<u>Filter Date</u>	<u>Number</u>	<u>Dust Load</u> mg	<u>Air Volume</u> m ³
3/1/1969	3500407	106.3	2124
19/1/1969	3500409	73.8	2172
4/2/1969	3500411	70.8	2196
20/2/1969	3500413	325.9	2154
8/3/1969	3500415	172.8	2100
31/3/1969	3500417	157.5	2020
Composite Filter (average)		151.1	2128

From the weight of the extraction residues, the composite Hi-Vol filter was estimated to contain about 6.0 mg organic material, which corresponds to 4.5% "organics" per weight of dust and about 3 mg "organics" per 1000 m³ air. The extraction efficiencies of the various solvents used are shown in Table 3.

TABLE 3
Soxhlet Extractions of Composite Hi-Vol Filter

Solvent	Boiling Point °C	Residue(dried at 25°C/80mm Hg/60 hrs) Corresp. to 1/12 filter	Residue(dried at 80°C/1 hr add'l)	"Organics" calc'd in 1000 m ³ air
		mg	mg	mg
n-Pentane	36	0.1	0.1	0.6
Iso-Octane	99	0.3	0.3	1.8
Cyclohexane	81	0.5	0.5	3.0
Benzene	80	0.6	0.5	3.0
Dioxane	101	35.9*	2.5 *	n.d.
Toluene	111	0.7	0.3	1.8

* The dioxane extract was believed to have given a misleading high result of "organics" owing to considerable water absorption on exposure to the atmosphere while the aliquote samples were taken. Difficulties were also encountered with n-pentane owing to its low boiling point of 36°C and the necessity of replacing evaporation losses.

From Table 3 it is apparent that the highest values for extracted "organics" were obtained with benzene and cyclohexane as the extractants. Therefore, these two solvents were judged to be superior to any other extractant tested in these experiments.

ii) Rate of Extraction

In order to establish the time required and the efficiency of various solvents for the extraction of polynuclear hydrocarbons from Hi-Vol filters, the rates of extraction were determined. For this purpose, aliquote samples (3 ml) were taken at certain time intervals during the Soxhlet extractions of the Hi-Vol filter composite. In each extraction, the size of the Hi-Vol filter composite corresponded to exactly half of a Hi-Vol filter; the amount of organic solvent used initially in each extraction was 80 ml; the total extraction time was about 12 hours with an estimated 42 Soxhlet cycles during this period.

The amounts of total polynuclear hydrocarbon compounds were determined by fluorescence measurements at the maximum excitation and emission wave lengths ($\lambda_{Ex} = 384$, $\lambda_{Em} = 425 \text{ nm}$). In accordance with results obtained earlier for the total "organics" in the extracts, the highest fluorescence intensities were found for the benzene and cyclohexane extracts while the extracts with the aliphatic solvents showed much weaker intensities. (Table 4 and Figure 2).

Although dioxane was initially the "fastest" extractant, its extraction rate decreased finally to the point where actually a loss of extracted material seemed to have taken place. This might be explained by the wide range of materials extracted with dioxane, which included also metallic and inorganic compounds and which in the presence of absorbed water and oxygen from the atmosphere could have given rise to reactions with the polynuclear hydrocarbons; these secondary reactions at the relatively high temperature of boiling dioxane could have led to oxygenated and other organic compounds and, thus, to a loss in fluorescence.

The rates of extraction (Figure 2) and the fluorescence of the final extracts (Table 4) show clearly the superiority of benzene and cyclohexane over the other solvents in the Soxhlet extractions of polynuclear hydrocarbons from Hi-Vol filters. The rates of extraction also indicate that for achieving quantitative extractions somewhat longer extraction times would be desirable. We suggest that the Soxhlet extractions should be maintained over approximately 18 hours instead of the 12 hour period used in this study.

Fluorescence
(Arbitrary Units)

$$\lambda_{Ex} = 384 \text{ nm (constant)}$$

$$\lambda_{Em} = 425 \text{ nm (measured)}$$

Hi-Vol Filter Extraction
Efficiency of Organic Solvents

Figure 2

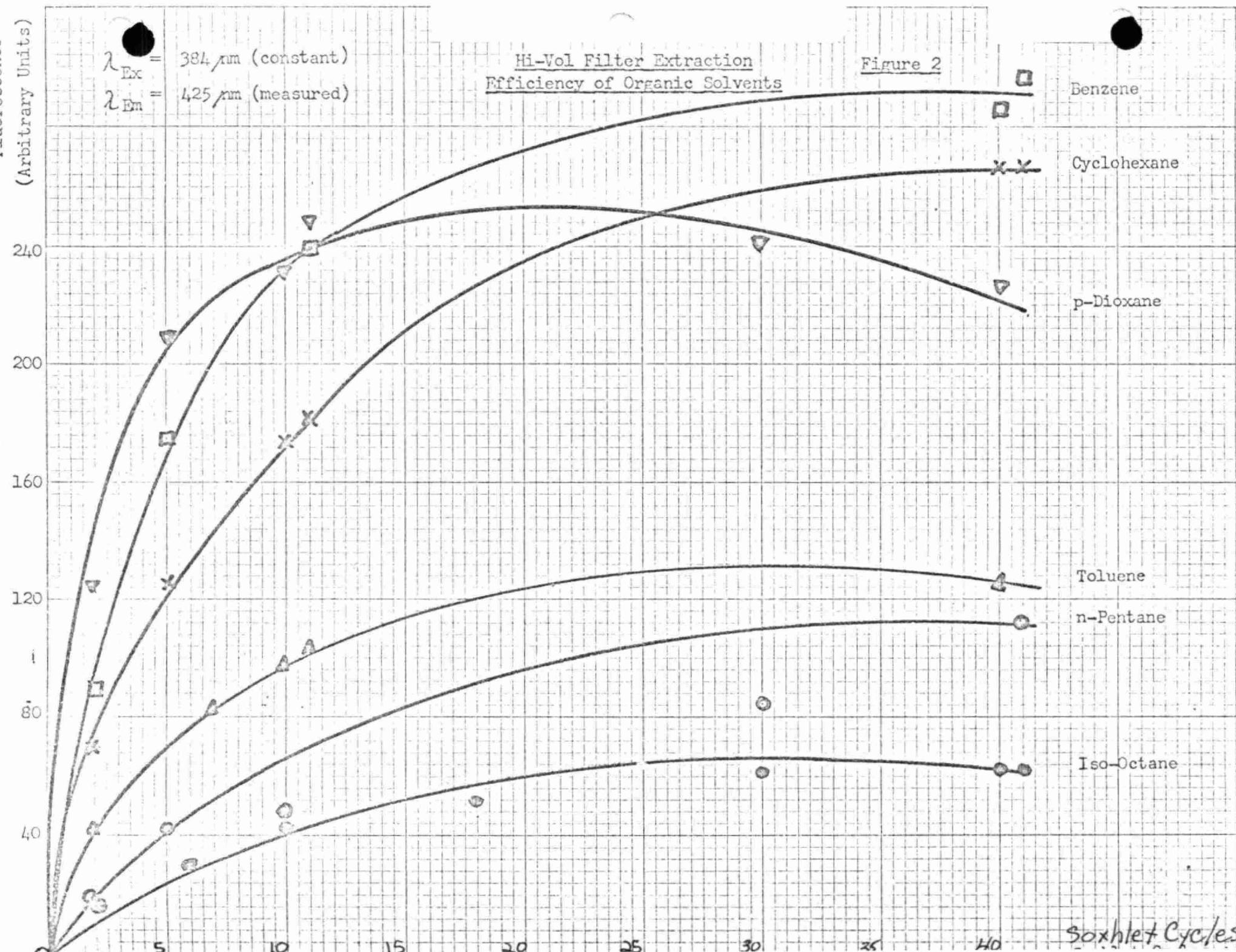


TABLE 4
Summary of Results from Soxhlet Extractions of Composite Hi-Vol Filter
with Various Organic Solvents (i)

Organics Extracted (mg/1000 m ³ air)	Polycyclics Extracted (Fluorescence, arb. u.)	BaP -Solubility (see Table 1)	BaP Extracted (ug/1000 m ³ air)	Extract Color
Benzene (3.0)	Benzene (285)	Benzene	Benzene (0.33)	Benzene
Cyclohexane (3.0)	Cyclohexane (267)	Toluene	Cyclohexane (0.33)	Toluene
Toluene (1.8)	Toluene (126)	Cyclohexane	Toluene (0.30)	Cyclohexane
Iso-Octane (1.8)	Pentane (113)	n-Hexane	Iso-Octane (0.28)	Dioxane
n-Pentane (0.6)	Iso-Octane (62)	n-Pentane	n-Pentane (0.20)	Iso-Octane
(ii)	(ii)	(ii)	Dioxane (0.14)	n-Pentane

(i) Sample size: $\frac{1}{2}$ Hi-Vol filter; Amount of solvent: 80 ml

(ii) For dioxane see footnote of Table 3.

iii) Benzo(a)Pyrene in Soxhlet Extracts

The amount of benzo(a)pyrene extracted from the composite Hi-Vol filter with various solvents were determined by fluorometry after chromatographic separation of BaP from the other components of the extracts. This procedure is outlined later in this report. As shown in Table 5, the amounts of BaP were found highest again when benzene and cyclohexane had been used as the extractants. Toluene gave slightly lower values, but the aliphatic solvents and dioxane proved to be much poorer extractants for BaP. The poor performance of dioxane as an extractant seemed to confirm that BaP underwent secondary reactions during the extraction with this solvent, as mentioned in the foregoing paragraph.

The observation that benzene and cyclohexane were the best extractants was in line with the practice of U.S. -- workers to use benzene and of Canadian workers to use cyclohexane as the preferred solvent. Accordingly, we decided to use cyclohexane for all Hi-Vol filter extractions henceforth.

TABLE 5

Benzo(a)Pyrene in Composite Hi-Vol Filter

Extractant	Number of Runs ⁽¹⁾	Average BaP/1000 m ³ Air μg ⁽²⁾
Cyclohexane	4	0.33
Benzene	6	0.33
Toluene	5	0.30
Iso-Octane	3	0.28
n-Pentane ⁽³⁾	2	0.20
p-Dioxane ⁽⁴⁾	2	0.14

(1) Independent chromatographic separations and fluorometric determinations.

(2) Uncorrected for possible benzo(k)fluoranthene interference.

(3) The low boiling point of n-pentane (36 C) contributed to the inefficiency of this solvent in the Soxhlet extraction.

(4) Water absorption from the air and co-extraction of inorganic components are believed to have resulted in reactions leading to a chemical change of some polycyclic hydrocarbons during the extraction.

iv) The Color of Hi-Vol Filter Extracts

During the investigations on Hi-Vol filter extraction the observation was made that depending on the organic solvent used as the extractant, the extract assumed a more or less yellow color. The intensity of the color seemed to correspond fairly closely with the amount of total polynuclear hydrocarbons extracted as measured by the fluorescence of the extract, and to similar extent with the concentration of benzo(a)pyrene (Table 4).

This relation of color intensity of the extract with BaP concentration does not only become apparent in extracts of Hi-Vol filters originating from the use of solvents with different efficiencies, but also in extracts of different Hi-Vol filters (with different BaP contents) by using the same solvent. We believe that the yellow color of these extracts is caused by compounds formed during condensation and carbonization processes of organic material as the result of incomplete combustions by which the polynuclear hydrocarbon compounds are formed. There seems little doubt that the color intensity of the Hi-Vol filter extracts could be used as a rough measure for the amount of polynuclear hydrocarbons on these filters.

Aiming at finding a faster and more convenient method for monitoring these compounds, this possibility was briefly investigated in a preliminary study during our survey of BaP and BkF in urban air in Ontario. From the Tables 10 to 17, it is abundantly apparent that the aforementioned relationship of extract color with polynuclear hydrocarbon concentration holds reasonably well and that hopes for developing an analytical method for these compounds, based on this relationship, seem well justified.

d) Extraction with the Use of Ultrasonic Dismembrator

Attempts were made to accomplish extraction of Hi-Vol filters with organic solvents at room temperature by the use of an ultrasonic dismembrator. By this technique it was hoped that it would be possible to avoid the high temperatures and long extraction times associated with Soxhlet extractions and thus avoid any possibility of a partial thermal degradation, or other chemical change, of the polycyclic aromatic compounds.

From the ultrasonic dismembrator used, energy was transmitted at about 20,000 cycles/sec. from a titanium tip of 0.5 in. diameter to the Hi-Vol filter suspended in a small volume of cyclohexane which was cooled at room temperature.

Within seconds the fabric of the filter portion desintegrated and a suspension of small fibres from the filter and of the absorbed particulate matter was obtained. When the solution or dispersion of all solid material appeared to be complete after 5 minutes of ultrasonic treatment, the suspension was filtered and the cyclohexane extract was subjected to the BaP and BkF analyses. A comparison of the results with those obtained after corresponding Soxhlet extractions is shown in Table 6.

TABLE 6
Comparison of Extraction Efficiencies -
Soxhlet versus Ultrasonics

Hi-Vol Filter			Soxhlet		Ultrasonics	
Station	Number	Date	BkF*)	BaP*)	BkF*)	BaP*)
Cornwall	56066	12/8/71	3.06	0.21	2.50	0.15
Hamilton	29008	12/8/71	2.60	1.02	1.27	0.63
North Bay	75020	13/8/71	0.12	0.07	0.10	0.06

*) $\mu\text{g}/1000 \text{ m}^3 \text{ air}$

The results in Table 6 demonstrate that the extraction by the ultrasonic dismembrator was incomplete at all levels of polynuclear hydrocarbon concentration tested. It appears that during the ultrasonic treatment mainly the larger particles were affected while the smaller remained unchanged at least partially. The short contact time of these particles at room temperature with the solvent did not permit sufficient penetration and elution of the soluble portions of these particles and, thus, the extraction remained only partially effective.

However, in view of the finding that the low temperature ultrasonic technique of extraction gave lower, and not higher, values for the polynuclear hydrocarbons, the Soxhlet extraction was considered to be superior in spite of the higher temperature to which these compounds were exposed; thus, the extent of thermal degradation, if any, during the Soxhlet extraction under the conditions used appears to be insignificant.

4) Chromatographic Separation of BaP and BkF

In order to be able to determine the amount of benzo(a)-pyrene or any other compound in Hi-Vol filter extracts by fluorometric analysis, it is necessary to separate this compound from all other compounds exhibiting similar fluorescence. Such compounds include a large number of the closely related polynuclear hydrocarbons whose presence would interfere with the analysis of BaP. As already mentioned, separation of these compounds can be accomplished by various procedures, usually involving column and thin layer chromatography, but which almost invariably are elaborate and time-consuming.

An exception to these lengthy procedures is a method, recently developed by Monkman and co-workers (11), according to which separation of BaP and BkF from all other organic compounds can be accomplished by chromatography within a relatively short time. Although by this method separation of the two compounds from each other is not accomplished, they successfully developed a fluorometric procedure by which the amounts of these compounds can be estimated with reasonable accuracy in most practical cases. We have selected this method, with some modifications, to serve as the basis for our present work. Mainly because of its speed and efficiency, compared with all other methods, this method

appeared to be the most suitable for larger scale surveys.

The chromatographic method, originally developed by Monkman's group, involves the following: A small sample of Hi-Vol filter extract is placed upon a short column of activated Peter Spence H-type alumina, and chromatographed by using anhydrous, spectrograde toluene as the liquid phase. The fractions emerging from the column, which contain BaP and BkF combined, are evaporated to small volume for the fluorometric analysis which is described in the next Section.

After having initially followed this method, we have introduced a number of minor modifications with the aim of improving the method by achieving better reproducibility and making it more suitable for routine analysis. A summary of the chromatographic conditions which we are using now is shown in Table 7. These conditions are being used now in our survey of BaP and BkF in urban air in Ontario, which is discussed later in this report.

Of the changes in the original method, we may mention the following: We were able to replace the expensive Peter Spence H-type alumina from England with ordinary, commercial

TABLE 7

Conditions for Liquid Phase Chromatography

Sample Size for Extraction: 1/10 of Hi-Vol Filter
Portion Taken for Analysis: $\frac{1}{2}$ of Extract (1/20 of Hi-Vol Filter)

This portion is evaporated in vacuo to 1.0 ml and applied onto the top of the alumina column.

Dimensions of Alumina Column: Length 140 mm
Diameter 13 mm
Alumina: "Fisher A-540", neutral activated at 140°C, mesh size 80 - 200.
Eluent: Toluene (Spectrograde), ca. 150 ml per run
Number of Fractions taken: 50
Fraction Size: 2.5 ml
Flow Rate: 50 - 60 sec. per fraction
Fraction Analyzed for BaP, EkF: From 8th to 48th fraction
Total Time Required: About 1 hour

alumina, such as supplied by Fisher Scientific. After conditioning at 140°C, this much cheaper alumina was found to be completely adequate and by its use even some occasional erratic column performance previously experienced could be eliminated. Also, rather than using the same column repeatedly, we obtained much better reproducibility after we began to use, on principle, a freshly prepared column for each chromatographic run. The fractions containing BaP and BkF were then obtained without tailing in less than 50 minutes, the total procedure including column preparation taking no more than 60 minutes. Great benefit was derived from the use of an automatic fraction collector with which up to 5 chromatographic separations were achieved simultaneously and which resulted in substantial time and labor savings. It was also found that the major part of the spectrograde toluene eluent could be recovered for further use by simply passing the used solvent through a column of Pittsburgh-type BPL activated carbon.

5) The Fluorometric Analysis of BaP and BkF

After obtaining both BaP and BkF, combined in the fractions from the chromatographic procedure just described, it is necessary to use Monkman's approximation method for fluorometrically estimating the amounts of each of these two compounds (11). According to this

method, the excitation wavelengths of 384 and 308 nm, respectively, are used which cause emission at 410 nm for both compounds; by measuring the emission intensities at this wavelength, the amounts of BaP and BkF in the fractions can be estimated from calibration curves of standard solutions, by calculation according to the following formulas:

$$\text{Conc. BkF} = \frac{\text{Emission (Sample)} \lambda \text{Ex 308 nm}}{\text{Slope (BkF Std.)} \lambda \text{Ex 308 nm}}$$

$$\text{Conc. BaP} = \frac{\text{Emission (Sample)} \lambda \text{Ex 384 nm} - [\text{Conc. BkF} \times \text{Slope(BkF Std.)}] \lambda \text{Ex 384 nm}}{\text{Slope (BaP Std.)} \lambda \text{Ex 384 nm}}$$

By programming these equations on computer cards for a desk computer, we not only eliminated the human error source in the calculations but also reduced the lengthy time period required for carrying out these calculations to less than 1 minute per complete analysis.

As the results from the analysis of synthetic mixtures of BaP and BkF show, this method proves to be fairly reliable in all cases in which the ratio BaP/BkF is smaller than 2. Only for mixtures with a ratio larger than 2, the above approximation technique by Monkman cannot be applied without introducing substantial errors in the results, a fact which was first mentioned in Monkman's

paper (11). However, it is also pointed out that according to recent experience, there is little danger that the ratio of these two compounds in filter extracts would often exceed this value. By analyzing a number of Hi-Vol filters by this method we found, generally, higher values for BkF than for BaP, which thus gave support to this latter statement.

Therefore, there was hardly a doubt that this method, being the most suitable available, would also be reasonably reliable for use in our subsequent survey of BaP and BkF in the air of major cities in Ontario.

6) New Method for Independently Determining BaP and BkF in Hi-Vol Filter Extracts

Although the estimation of BaP and BkF by the "Monkman Method" results in close approximation to the true values for most Hi-Vol filter extracts, one primary aim in our work remained the independent and accurate determination of these compounds by a direct method. Such a method would not only provide the means of checking the accuracy of Monkman's approximation technique, but would permit also the accurate determination of all Hi-Vol filter extracts regardless whether the BaP content should be present in large excess over BkF or not.

Aiming at developing such a method, we undertook an extensive search for chromatographic conditions under which BaP and EkF would separate from the remainder of the organic material as well as from each other. In the course of this work, we have discovered a procedure by which such a separation became possible in a one-step chromatographic operation, which thus enabled us to determine these two compounds in such direct manner for the first time.

The following is a brief outline of this procedure: Of a large variety of column packings tried, we found that only a certain type of high-quality alumina with a narrowly defined activity range would give separation of BaP and EkF. The alumina is WOELM 101 - Alumina, Brockman Activity 1, pH - value 7.5, which is transferred from its factory-sealed metal container directly into a humidity chamber for deactivation to the exact degree required. For achieving satisfactory separation of these two hydrocarbons, conditioning of the alumina at 60% humidity for a period of 90 minutes at room temperature is necessary. A saturated solution of aqueous magnesium nitrate can be used for adjusting the chamber to the above humidity. After completion of the conditioning, the alumina is immediately used

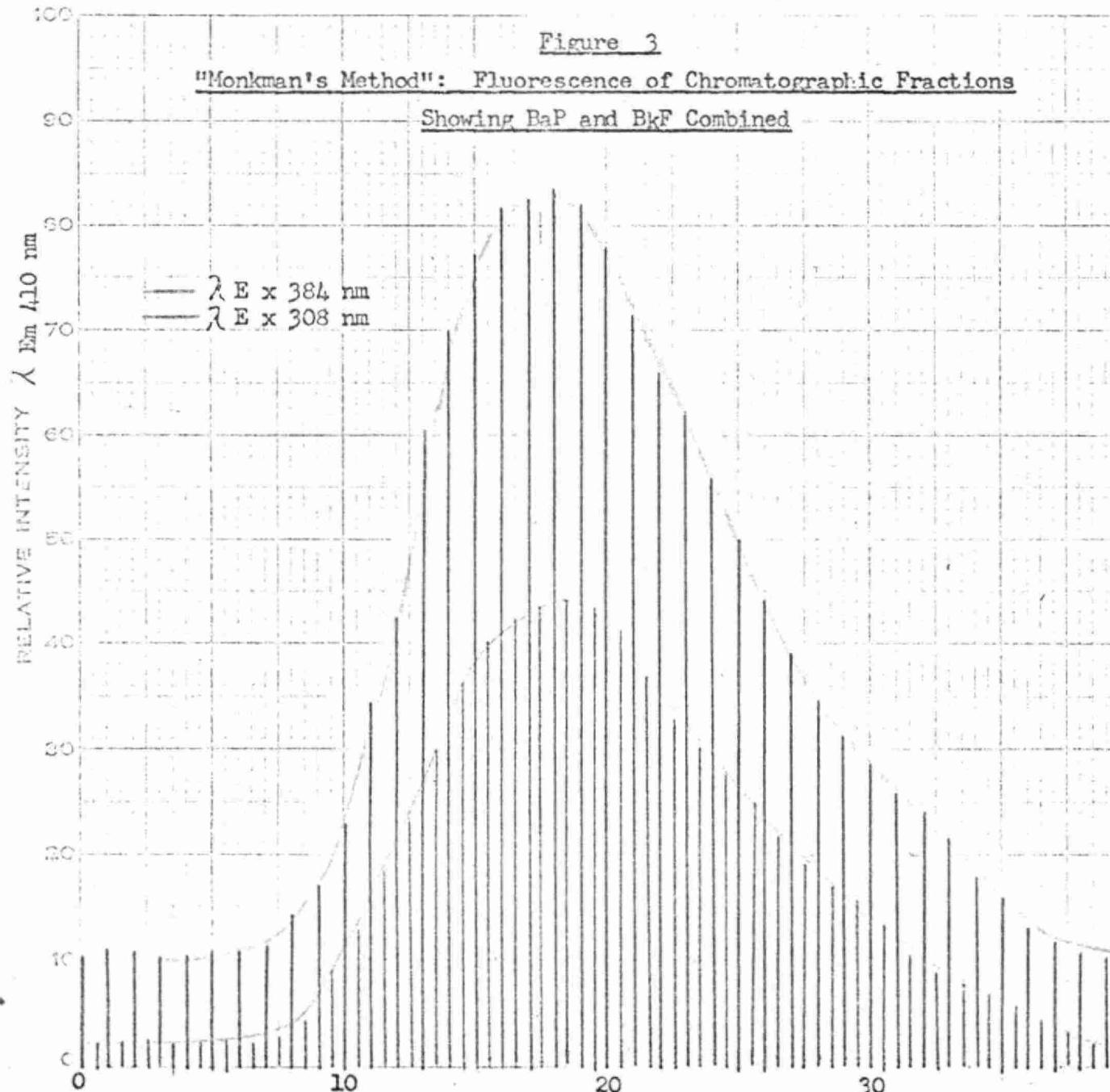
for making up a slurry with anhydrous toluene (nanograde), with which a chromatographic column of 100 mm height is prepared. Any deviation from this procedure with regard to type of alumina, deactivation and column preparation would almost certainly reduce or prevent any separation or would lead to prohibitive long column retention times.

After application of a small extract sample (about 0.1 to 1 ml) onto the top of the chromatographic column and by using toluene (nanograde) as the liquid phase, benzo(a)pyrene is the first to elute from the column (in Fractions 11 to 25), which then is followed by benzo(k)fluroanthene (in Fractions 25 to 53, each fraction containing 2.5 ml). These fractions, as obtained by an automatic fraction collector, are tested by fluorometry for their BaP and BkF contents. By subjecting each of them to excitations at the selective wavelengths for BaP and BkF (384 nm and 308 nm, respectively), the patterns of the emission intensities at 410 nm reflect clearly the complete separation of these two compounds. We believe that quantitative determination of these compounds can simply be done by integration of the peak areas and by relating the results to those obtained by standard mixtures.

EXCITATION & EMISSION SPECTRA
AURORAY INSTRUMENT CO., INC.
2700 REED RD. RD. #1, SILVER SPRING, MARYLAND, U.S.A.

Figure 3

"Monkman's Method": Fluorescence of Chromatographic Fractions
Showing BaP and BkF Combined



EXCITATION & EMISSION SPECTRA

SAMPLE: BaP + BkF (synth. mixture)

SOLVENT: Toluene

CONCENTRATION: 0.05+0.05 ug

TIME: 0.003 SENSITIVITY: 25 PM TIME: R446S

LIGHT: Xenon TEMP. R.T. °K

DATE: Nov. 1971 OBSERVER: W.O.

SLIT $\frac{\text{mm}}{\text{cm}}$ SHUTTER PORTS

A 1 F 1 GLENNING

B 8 C 2 R.P.M.

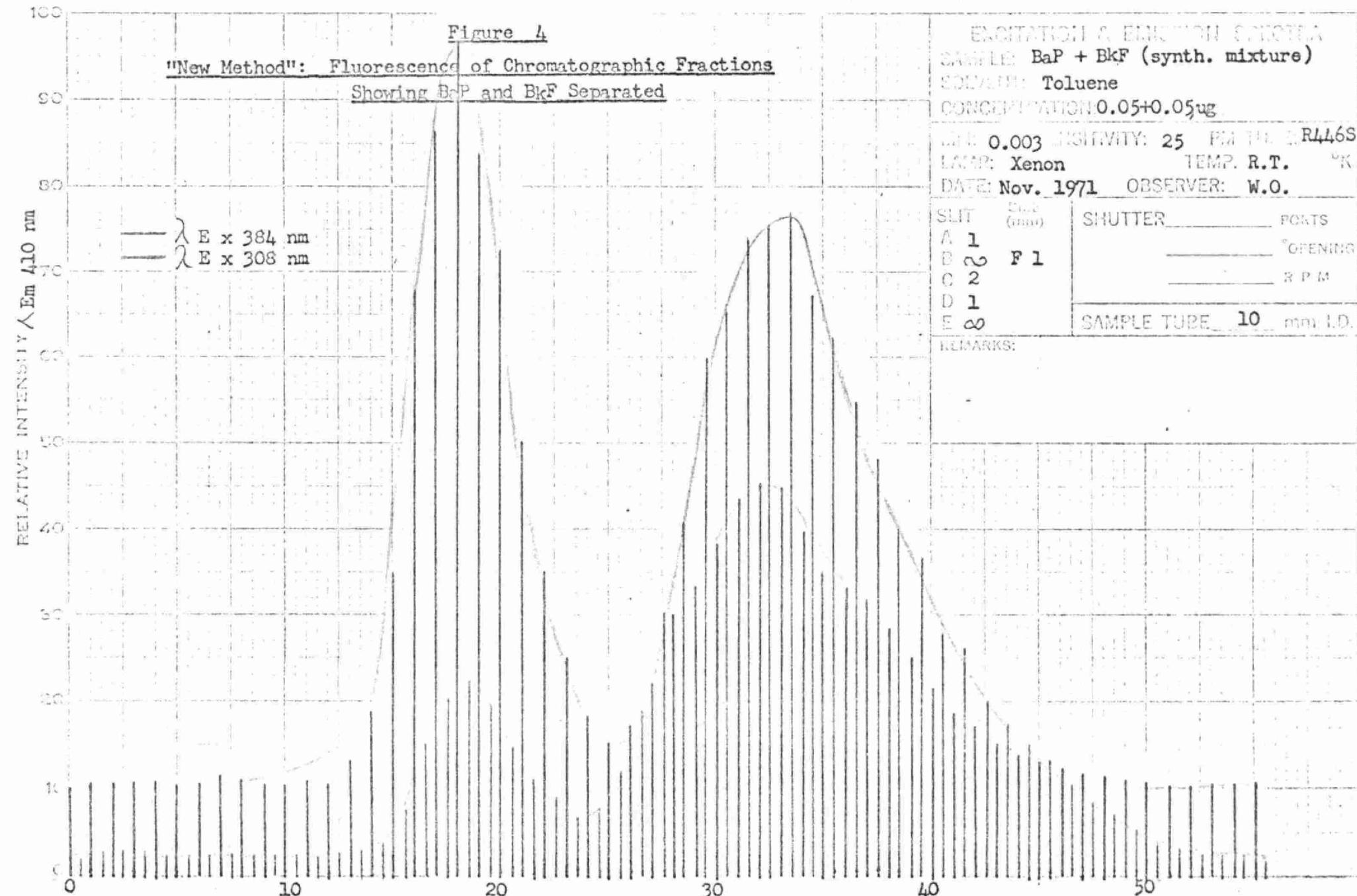
D 1 E 8 SAMPLE TUBE 10 mm I.D.

REMARKS:

THE MARYLAND PAPER
MOUNTAIN MINE CO., INC.
TOWSON, MARYLAND, U.S.A.

Figure 4

"New Method": Fluorescence of Chromatographic Fractions
Showing B₁P and BkF Separated



**EXCITATION & EMISSION SPECTRA
SAMPLE BaP + BkF (synth. mixture)**

Solvent: Toluene

CONCENTRATION 0.05+0.05 ug

LAM 0.003 VISIBILITY: 25 KM THICK R446S
LAMP: Xenon TEMP. R.T. °K
DATE: Nov. 1971 OBSERVER: W.O.

SLIT	Size (mm)	SHUTTER	PORTS
A	1		% OPENING
B	2	F 1	
C	2		R P M
D	1		
E	8	SAMPLE TUBE	10 mm I.D.

REMARKS

Figures 3 and 4 give an illustration of the results obtained from a synthetic mixture of BaP and BkF (0.05 μ g each) by using Monkman's conditions and by the new method, respectively. When the first named conditions are used no separation of these two compounds from each other had occurred, while by our method complete separation was accomplished.

Similar results were obtained when actual Hi-Vol filter extracts were used, as shown in Figures 5 and 6. By Monkman's technique, BaP and BkF were separated from the remainder of the organic material in the extracts but they remained unseparated from each other as if they were a single compound. By contrast, good separation of these two compounds was achieved with the new method.

For greater sensitivity of this method and at the same time for reducing the number of fluorometric measurements, the fractions containing a single hydrocarbon compound can be combined for evaporation to small volume in vacuo, the emission intensity of the concentrate being directly indicative of the total amount

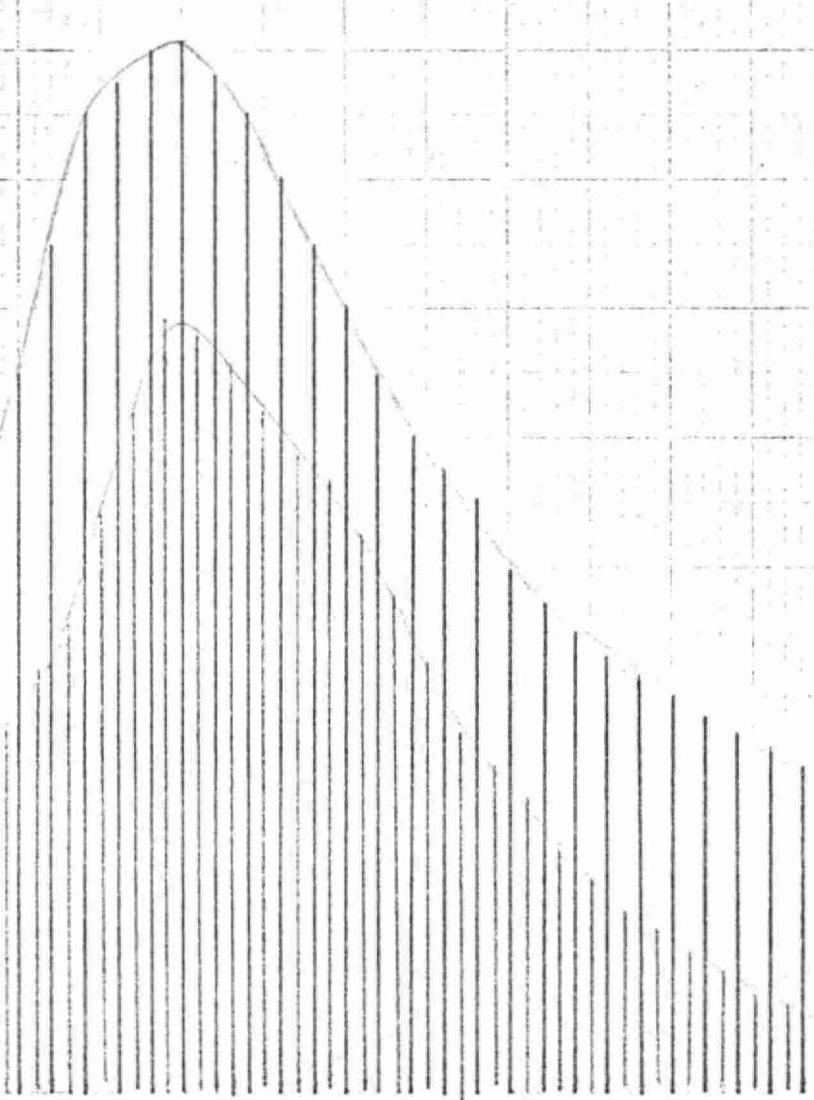
MONKMAN'S METHOD FOR POLYCYCLIC AROMATIC HYDROCARBONS
A MONKMAN RESEARCH COMPANY
1000 University Avenue, Baltimore, Maryland, U.S.A.

Figure 5

"Monkman's Method": Separation of Hi-Vol Filter Extract
Showing BaP and BkF Combined

RELATIVE INTENSITY λ_{Em} 410 nm

— λ E x 384 nm
— λ E x 308 nm



EMISSION & ABSORPTION SPECTRA

SAMPLE: Hi-Vol Filter

CARRIER: Toluene

CONCENTRATION: 20

WAVELENGTH: 0.003 INSTRUMENT: 25 PHOTOMETER: R446S

LAMP: Xenon TEMP: R.T. °K

DATE: Nov. 1971 OBSERVER: W.O.

WAVELENGTH (nm)	SHUTTER	10.13
A 1	OPENING	P.P.M.
B ∞	F 1	
C 2		
D 1		
E 8		

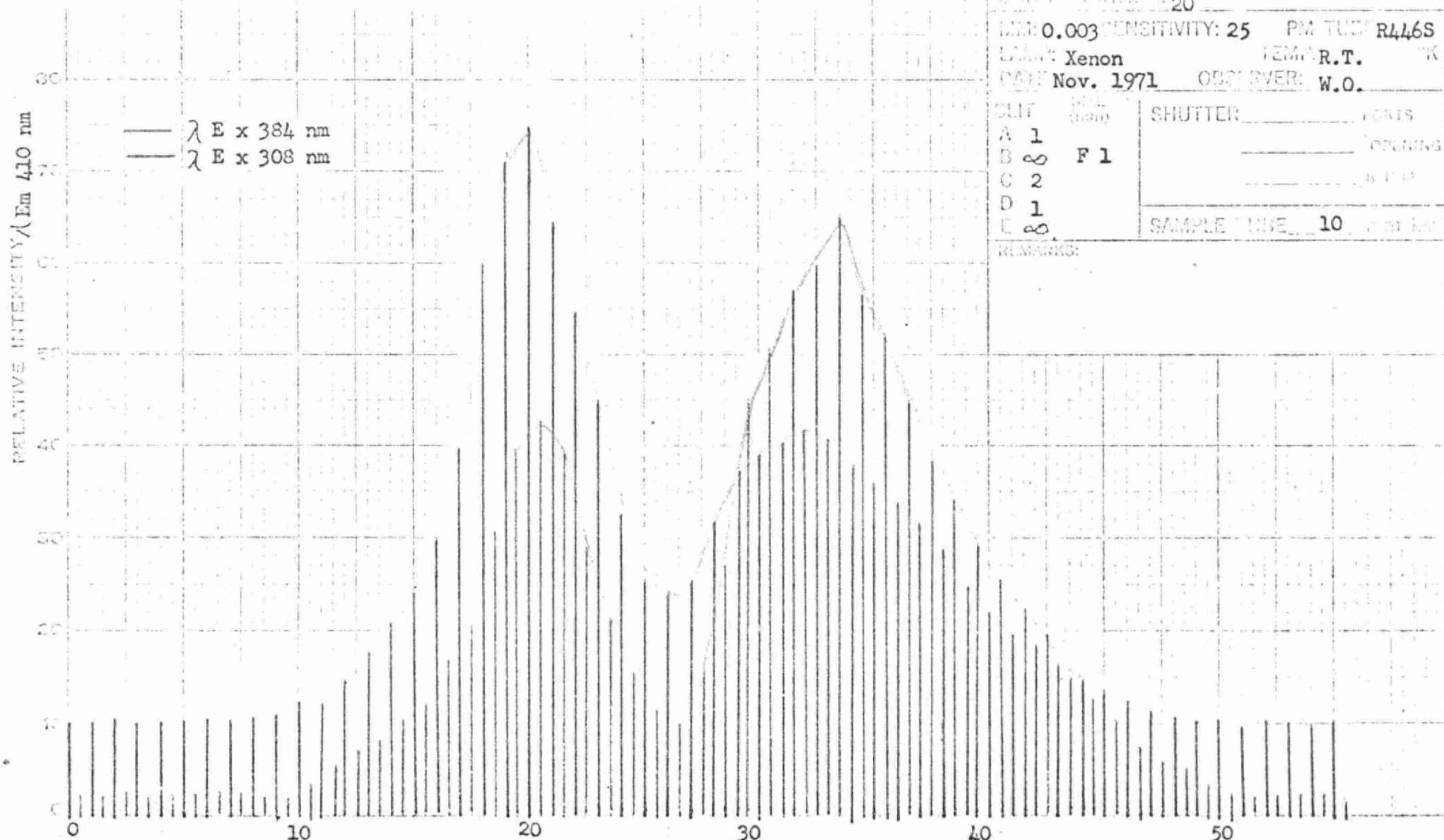
SAMPLE TUBE	10 mm I.D.
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REFERENCE	
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CHART OF ABSORPTION SPECTRUM
AND SENSITIVITY CHART
FARQUHAR HIGH-VOLUME CO., INC.
1000 UNIVERSITY SPRINGS, MARYLAND, U.S.A.

Figure 6

"New Method": Separation of Hi-Vol Filter Extract
Showing BaP and BkF Separated



EXCITATION & LIFE SPAN SPECTRA

CHAMBER: Hi-Vol Filter

SOLVENT: Toluene

EXPOSURE TIME: 1 Filter
20

MM 0.003 SENSITIVITY: 25 PM TUBE R446S

LIGHT: Xenon TEMP: R.T. °K

DATE Nov. 1971 OBSERVER: W.O.

SLIT (mm) SHUTTER (mm)

A 1 F 1 OPENING

B ∞ C 2

D 1 E ∞

SAMPLE TUBE: 10 mm

REMARKS:

of each compound in the extract. Therefore, calculation of the analytical results is a straightforward matter and does not involve the use of elaborate approximation formulas as otherwise required.

A comparison of the two methods is shown in Table 8. The analytical results obtained by using these methods on mixtures containing known amounts of BaP and BkF, demonstrate that reasonable accuracy can be achieved with both methods except when the amount of BaP exceeds that of BkF. This restriction, however, does not apply when the "new method" is used, which was to be expected after separation of these two compounds made individual analysis of each compound possible. This wider applicability of the "new method" represents a definite advantage over "Monkman's method", although - as already mentioned - the extended range might be of only limited importance for the analysis of most Hi-Vol filter extracts.

Another advantage of the new method could be its convertibility to continuous operation of the fluorometric measurements of the column effluents. With continuous fluorometric measurement of the column effluent, a further simplification of the method, optimization of fluorometer use and considerable savings in manual labor could be realized.

Table 8

Comparison of "Monkman's Method" and the "New Method".

Synthetic Mixture		'Monkman's Method'		'New Method'	
μgBaP	μgBkF	μgBaP	μgBkF	μgBaP	μgBkF
0.050	0.050	0.049	0.061	.049	0.048
0.025	0.075	0.025	0.080	.022	0.076
0.075	0.025	0.060	0.041	.073	0.024

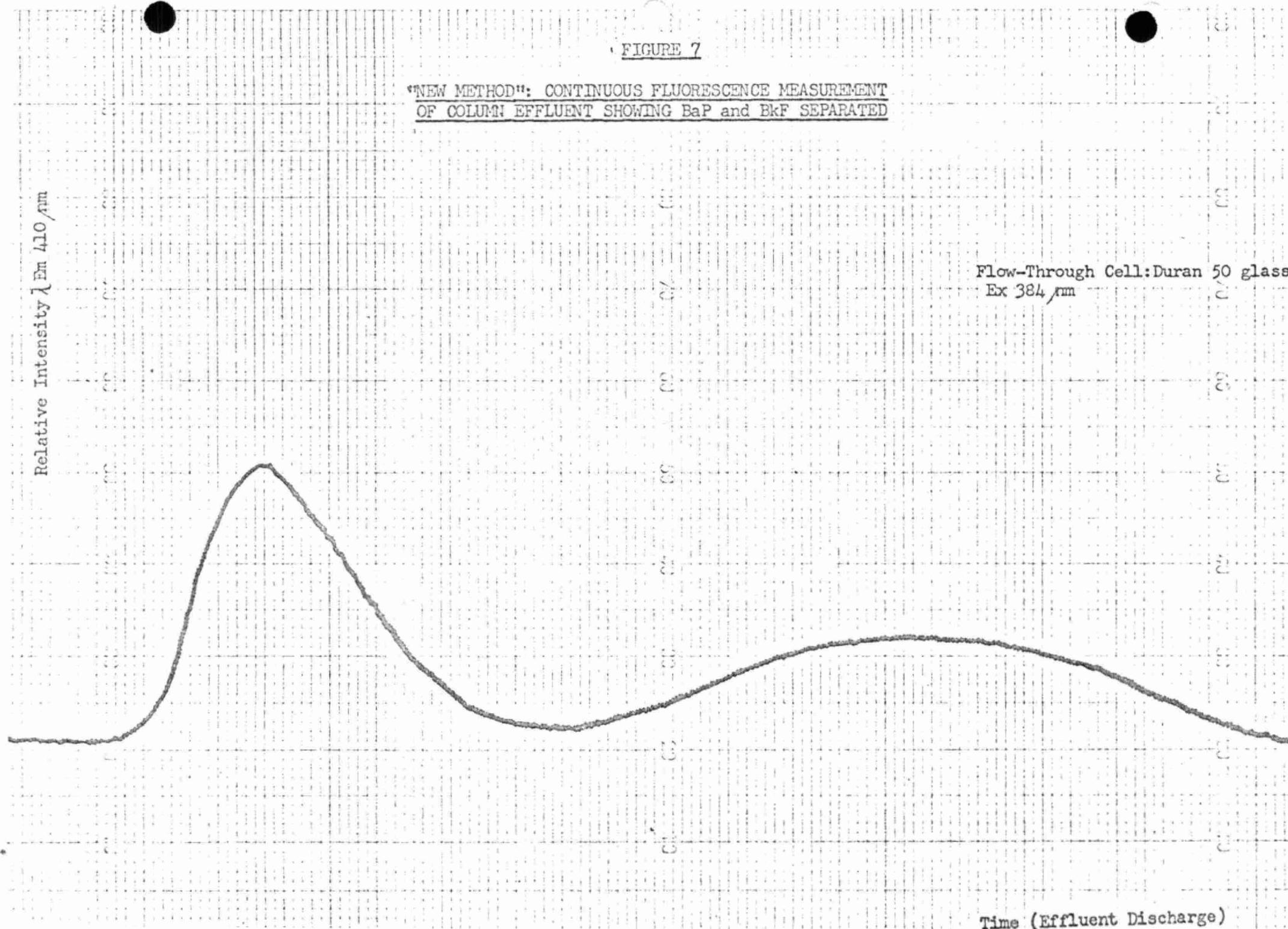
We have tested the potential of the "new method" for conversion to such continuous operation. Since we had not yet received the required quartz flow - through cell for our preliminary investigation, we had to improvise with one made of ordinary glass. This precluded the use of the short wavelength of 308 nm for the excitation of BkF, and as a compromise, the longer BaP wavelength at 384 nm was used for both compounds.

Nevertheless, as shown in Figure 7, the chromatographic separation of BaP and BkF (0.05 μ g each) from a synthetic mixture was nearly perfect and the amounts of these two compounds could readily be monitored by the continuous measuring of the emission at 410 nm. Of course, much greater sensitivity will be attained for the BkF response, when the quartz flow-through cell becomes available which will permit the use of the appropriate excitation wavelengths. A minor difficulty which might be mentioned could be the necessity to change to the correct attenuation prior to the fluorometric monitoring to permit integration of the area undisturbed by attenuation changes. By using an electronic integrator (about \$3,500), the attenuation would automatically be adjusted while integration of the area would proceed to give the final result on the print-out. If such an integrator is not available, occasional

FIGURE 7

"NEW METHOD": CONTINUOUS FLUORESCENCE MEASUREMENT
OF COLUMN EFFLUENT SHOWING BaP and BkF SEPARATED

Relative Intensity λ_{Em} 410 nm



Flow-Through Cell:Duran 50 glass
Ex 384 nm

Time (Effluent Discharge)

repeats of the chromatographic runs with the corresponding losses in time and labor may be necessary, especially if there are wide variations of BaP and BkF concentrations in Hi-Vol filter extracts.

Upon completion of this development work, we expect to have ready an alternative to Monkman's method for the quantitative determination of BaP and BkF. We are hopeful that this new method will show improvements over the other in accuracy, applicability and simplicity.

7) Survey of BaP and BkF in Urban Atmospheres in Ontario

a) Selection of Hi-Vol Stations

After our methods development programme for determining BaP and BkF in Hi-Vol filter extracts was sufficiently advanced for enabling us to conduct reasonably fast and reliable analyses, we embarked on a survey of these compounds in urban atmospheres in Ontario. As a first target, a one-year survey covering a number of industrial and urban areas was planned, where this type of air pollutants was believed to be most prevalent.

In accordance with our instrumental and manpower capability and after consultation with Dr. M. Fitch (Medical Consultant, A.M.B.), six stations were selected with the corresponding Hi-Vol filters to be analyzed on a bi-weekly basis commencing in July 1971. In addition to these stations, we were also able to include Ottawa and North Bay in our survey. These eight stations and the reasons for their selection are shown in Table 9.

TABLE 9

Stations of Hi-Vol Filters Used in Survey

Location	Station #	Reason for Selection
Sarnia (Front & Lochiel)	14051	Petrochemical Industry
North Bay (Teacher's College)	75020	"Background" Level for BaP
Toronto (Hy.401 & Pharmacy)	33002	Heavy Traffic (ground level)
Toronto (College St.)	31001	Ambient City Air
Ottawa (McDonald Garden)	51001	Capital (some local industry)
Windsor (University Ave.)	12008	Neighbouring Detroit's Industry
Hamilton (North Park Ave.)	29008	Heavy Industry (known high BaP)
Cornwall (Post Office Bldg.)	56066	Industry (known high BaP)

b) Results of Survey To-date

Analytical results covering a 5-months period (starting with July 3, 1971) are now available for the levels of BaP and BkF on Hi-Vol filters from the stations selected. The results shown in Tables 10 to 17 include the values for these compounds per unit air-volume and dust-weight. In addition, the extract color intensities had been obtained for the purpose of studying their relationship with BaP and BkF concentrations; it is hoped that such a study might provide a basis for development of a faster analytical method.

c) Comments to Results of Survey

In view of the present incompleteness of our survey it would appear that any conclusions from the results obtained until now may be premature. However, we think that the following observations and preliminary remarks are in order, inspite of the early stage of this study:

TABLE 10

Benzo(k)Fluoranthene and Benzo(a)Pyrene on Hi-Vol Filters

Station: SARNIA

Number: 14051

Hi-Vol Filter					BkF per 1 gram Dust ug	BaP per 1 gram Dust ug	Color 1) of Extract	BkF per 1000m ³ Air ug	BaP per 1000m ³ Air ug
Date (1971)	Number	Dust mg.	Air m ³	Sampling Day					
3/7	99	213.8	2330	Sat.	1.21	0.17	4	0.11	0.02
19/7	101	169.1	2521	Mon.	2.17	0.40	4	0.15	0.03
27/7	102	202.8	2440	Tue.	1.98	1.59	4	0.16	0.13
12/8	104	226.2	2305	Thur.	3.28	2.05	3	0.32	0.20
28/8	106	182.7	2411	Sat.	1.37	0.99	4	0.10	0.07
13/9	108	215.5	2411	Mon.	1.12	0.37	4	0.10	0.03
29/9	110	324.3	2411	Wed.	0.76	0.37	4	0.10	0.05
15/10	112	544.4	2440	Fri.	1.49	1.24	2	0.33	0.28
31/10	114	257.9	2521	Sun.	2.48	2.28	2	0.25	0.23
16/11	116	362.4	2493	Tue.	1.63	1.61	2	0.24	0.23
2/12	118	198.4	2442	Thur.	6.21	8.76	2	0.50	0.71

1) Color intensity decreasing from 1 to 4 (yellow to colorless).

TABLE 11

Benzo(k)Fluoranthene and Benzo(a)Pyrene on Hi-Vol Filters

Station: NORTH BAY

Number: 75020

Hi-Vol Filter					BkF per 1 gram Dust / μ g	BaP per 1 gram Dust / μ g	Color 1) of Extract	BkF per 1000m ³ Air / μ g	BaP per 1000m ³ Air / μ g
Date (1971)	Number	Dust mg.	Air m ³	Sampling Day					
4/7	99	175.0	2334	Sun.	13.9	5.27	2	1.04	0.39
20/7	n.a. ²⁾	-	-	-	-	-	-	-	-
28/7	102	125.9	2289	Wed.	4.75	4.02	4	0.26	0.22
13/8	129	88.4	2505	Fri.	3.47	1.90	4	0.12	0.07
28/8	128	138.2	2436	Sat.	3.73	2.54	4	0.21	0.14
13/9	130	114.6	2437	Mon.	1.84	1.18	4	0.09	0.06
29/9	132	111.2	2317	Wed.	6.18	1.63	4	0.30	0.08
15/10	134	265.0	2387	Fri.	3.02	2.05	3	0.34	0.23
31/10	136	108.7	2436	Sun.	5.34	6.22	4	0.24	0.28
16/11	138	114.3	2579	Tue.	13.9	5.97	2	0.62	0.26
2/12	140	61.0	2556	Thur.	5.91	7.82	4	0.14	0.19

1) Color intensity decreasing from 1 to 4 (yellow to colorless).

2) Hi-Vol filter not available.

TABLE 12

Benzo(k)Fluoranthene and Benzo(a)Pyrene on Hi-Vol Filters

Station: TORONTO-Hwy 401 Number: 33002

Hi-Vol Filter					BkF per 1 gram Dust / μ g	BaP per 1 gram Dust / μ g	Color 1) of Extract	BkF per 1000m ³ Air / μ g	BaP per 1000m ³ Air / μ g
Date (1971)	Number	Dust mg.	Air m ³	Sampling Day					
3/7	n.a. ²⁾	-	-	-	-	-	-	-	-
11/7	65	196.6	2468	Sun.	3.15	0.66	3	0.25	0.05
27/7	n.a. ²⁾	-	-	-	-	-	-	-	-
20/8	70	314.6	2175	Fri.	2.49	1.69	4	0.36	0.24
28/8	71	244.8	2130	Sat.	3.92	2.63	2	0.45	0.30
13/9	73	237.3	2020	Mon.	3.63	3.76	3	0.43	0.44
29/9	75	288.2	2199	Wed.	5.18	1.15	4	0.68	0.15
15/10	77	347.6	2132	Fri.	3.16	3.87	3	0.52	0.63
31/10	79	208.9	2219	Sun.	5.09	4.22	3	0.48	0.40
16/11	81	331.2	2199	Tue.	5.65	4.44	2	0.85	0.67
2/12	83	331.5	2109	Thur.	6.92	6.83	2	1.09	1.07

1) Color intensity decreasing from 1 to 4 (yellow to colorless).

2) Hi-Vol filter not available.

TABLE 13

Benzo(k)Fluoranthene and Benzo(a)Pyrene on Hi-Vol FiltersStation: TORONTO-College St. Number: 31001

Hi-Vol Filter					BkF per 1 gram Dust / μ g	BaP per 1 gram Dust / μ g	Color 1) of Extract	BkF per 1000m ³ Air / μ g	BaP per 1000m ³ Air / μ g
Date (1971)	Number	Dust mg.	Air m ³	Sampling Day					
3/7	639	157.2	2195	Sat.	1.92	0.80	3	0.14	0.06
19/7	655	186.9	2558	Mon.	3.62	1.01	3	0.26	0.07
27/7	663	134.7	2175	Tue.	3.06	1.86	4	0.19	0.12
12/8	279	196.1	2226	Thur.	2.22	3.25	3	0.20	0.29
28/8	766	152.4	2321	Sat.	2.36	1.39	3	0.16	0.09
13/9	694	163.5	2081	Mon.	2.54	1.88	3	0.20	0.15
29/9	711	325.9	2170	Wed.	4.47	2.00	2	0.67	0.30
15/10	726	444.3	2166	Fri.	4.15	3.78	2	0.85	0.78
31/10	742	257.9	2334	Sun.	5.21	1.02	2	0.58	0.11
16/11	772	334.6	2215	Tue.	7.52	5.01	2	1.14	0.76
2/12	788	165.7	2122	Thur.	6.35	8.70	2	0.50	0.68

1) Color intensity decreasing from 1 to 4 (yellow to colorless).

TABLE 14

Benzo(k)Fluoranthene and Benzo(a)Pyrene on Hi-Vol Filters

Station: OTTAWA

Number: 51001

Hi-Vol Filter					BkF per 1 gram Dust / μ g	BaP per 1 gram Dust / μ g	Color 1) of Extract	BkF per 1000m ³ Air / μ g	BaP per 1000m ³ Air / μ g
Date (1971)	Number	Dust mg.	Air m ³	Sampling Day					
3/7	59	126.0	2428	Sat.	1.73	1.45	4	0.09	0.03
18/7	64	166.0	2133	Sun.	0.97	0.87	4	0.08	0.07
27/7	68	239.0	2362	Tue.	0	23.7	3	-	2.40
11/8	72	166.0	2525	Wed.	1.47	1.57	4	0.10	0.10
29/8	78	186.0	2476	Sun.	33.6	104.0	3	2.53	7.82
13/9	83	226.0	2362	Mon.	1.77	1.40	4	0.17	0.13
28/9	88	391.6	2440	Tue.	10.6	6.61	1	1.70	1.06
16/10	94	187.7	2387	Sat.	4.31	2.60	3	0.34	0.20
31/10	98	335.2	2362	Sun.	3.58	5.34	3	0.51	0.75
15/11	104	220.4	2387	Mon.	16.8	10.8	1	1.55	1.00
3/12	110	98.7	2415	Fri.	3.34 104	2.62 214	3	0.17 4.24	0.17 8.75

1) Color intensity decreasing from 1 to 4 (yellow to colorless).

TABLE 15

Benzo(k)Fluoranthene and Benzo(a)Pyrene on Hi-Vol Filters

Station: WINDSOR

Number: 12008

Hi-Vol Filter					BkF per 1 gram Dust / μ g	BaP per 1 gram Dust / μ g	Color 1) of Extract	BkF per 1000m ³ Air / μ g	BaP per 1000m ³ Air / μ g
Date (1971)	Number	Dust mg.	Air m ³	Sampling Day					
6/7	94	200.3	2105	Tue.	2.58	0.78	4	0.25	0.07
15/7	97	395.4	2032	Thur.	21.6	16.4	1	4.21	3.18
27/7	101	357.6	2196	Tue.	8.46	2.13	1	1.38	0.35
11/8	106	645.0	2301	Wed.	23.1	10.0	1 (+)	6.47	2.81
29/8	112	268.1	2554	Sun.	4.28	2.49	4	0.45	0.26
13/9	117	245.7	2456	Mon.	3.35	2.53	3	0.34	0.25
1/10	123	368.3	2550	Fri.	3.22	1.99	3	0.47	0.29
16/10	128	346.7	2199	Sat.	4.00	1.39	2	0.63	0.22
31/10	133	299.4	2599	Sun.	12.7 11.9	8.06	3	1.37	0.93
15/11	138	696.4	2224	Mon.	13.6	10.5	1	4.26	3.28
3/12	144	714.3	2175	Fri.	32.6	33.3	1 (+)	10.7	10.9

1) Color intensity decreasing from 1 to 4 (yellow to colorless).

TABLE 16

Benzo(k)Fluoranthene and Benzo(a)Pyrene on Hi-Vol Filters

Station: HAMILTON

Number: 29008

Hi-Vol Filter					BkF per 1 gram Dust /ug	BaP per 1 gram Dust /ug	Color 1) of Extract	BkF per 1000m ³ Air /ug	BaP per 1000m ³ Air /ug
Date (1971)	Number	Dust mg.	Air m ³	Sampling Day					
3/7	72	237.2	2048	Sat.	1.55	0.37	4	0.18	0.04
19/7	74	256.8	2093	Mon.	1.62	1.25	3	0.20	0.15
27/7	76	204.3	2183	Tue.	24.8	10.5	1	2.32	0.98
12/8	78	376.3	2183	Thur.	15.1	5.93	1	2.60	1.02
28/8	80	158.1	2183	Sat.	2.63	1.12	4	0.19	0.08
13/9	83	124.9	2183	Mon.	2.01	1.27	4	0.12	0.07
29/9	87	367.9	2158	Wed.	31.5	23.6	1	5.38	4.02
15/10	91	468.3	2113	Fri.	19.8	9.18	2	4.39	2.03
31/10	95	362.0	2224	Sun.	31.0	25.1	1	5.05	4.08
16/11	99	125.1	2248	Tue.	3.97	4.35	3	0.22	0.24
28/11	102	469.0	2224	Sun.	29.5	32.7	1	5.18	6.90

1) Color intensity decreasing from 1 to 4 (yellow to colorless).

TABLE 17

Benzo(k)Fluoranthene and Benzo(a)Pyrene on Hi-Vol Filters

Station: CORNWALL

Number: 56066

Hi-Vol Filter					BkF per 1 gram Dust / μ g	BaP per 1 gram Dust / μ g	Color 1) of Extract	BkF per 1000m ³ Air / μ g	BaP per 1000m ³ Air / μ g
Date (1971)	Number	Dust mg.	Air m ³	Sampling Day					
3/7	30	586.8	2060	Sat.	11.5	1.20	1	3.28	0.30
19/7	32	151.5	2061	Mon.	50.5	5.34	2	3.71	0.39
27/7	33	127.4	2106	Tue.	13.0	0.58	4	0.79	0.04
12/8	35	120.6	2081	Thur.	52.8	3.56	3	3.06	0.21
28/8	37	642.1	1877	Sat.	39.0	7.27	1	13.3	2.48
13/9	n.a. ²⁾	-	-	-	-	-	-	-	-
29/9	39	191.8	1840	Wed.	45.2	10.9	2	4.71	1.13
7/10	40	78.4	1644	Thur.	3.16	1.88	4	0.15	0.09
31/10	n.a. ²⁾	-	-	-	-	-	-	-	-
15/11	n.a. ²⁾	-	-	-	-	-	-	-	-
3/12	n.a. ²⁾	-	-	-	-	-	-	-	-

1) Color intensity decreasing from 1 to 4 (yellow to colorless).

2) Hi-Vol filter not available.

i) An inspection of Tables 10 to 17 reveals that generally low levels of BaP and BkF are present in the Hi-Vol filters of the following stations (in the order of slightly increasing values): Sarnia, North Bay, Toronto (Hy. 401) and Toronto (College St.). Fairly high levels - at least occasionally - are found for the other stations (also with increasing values): Ottawa, Windsor, Hamilton and Cornwall.

In Table 18, suggestions as to the possible reasons for the levels found are shown, which may deserve further investigations regarding their validity after this survey is completed.

TABLE 18

<u>Station¹⁾</u>	<u>Possible Reasons for Observed BaP - BkF Levels</u>
Sarnia	Station located up-wind from industry? Petrochemical emissions: Generally low values?
North Bay	Non-industrial: Low values
Toronto (Hy.401)	Automotive emissions: Generally low values?
Toronto (College St.)	Ambient city air at 6 floors' height: Low values
Ottawa	Neighbouring paper company(?): Occasional high values
Windsor	Down-wind from Detroit's Industry: High values
Hamilton	Heavy industry, power plants: High values
Cornwall	Industry (paper industry?): High values

1) In order of generally increasing BaP - BkF levels.

- ii) With few exceptions, the values for BkF are found to be higher than those for BaP.
- iii) Higher BaP - BkF values can usually be expected when higher color intensities of the filter extracts are observed.
- iv) The amount of dust on Hi-Vol filters does not seem to permit any conclusions on the levels of BaP and BkF in the air.
- v) The effect which the day of the week may have on the BaP - BkF levels is still unclear; it may have some local significance. Seasonal effects cannot yet be estimated.
- vi) In the progress of this work with more data becoming available, more inter-relationships of environmental circumstances with the observed BaP - BkF values are expected to become apparent. Also, we hope to be able to include other important urban areas in Ontario in our survey. After completion of this survey, we plan to issue a further report on this study.

8) Acknowledgements

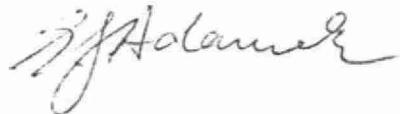
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